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(54) Toner For Developing Electrical Latent Image

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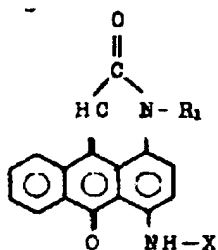
A Detailed Description

1. Title of the invention

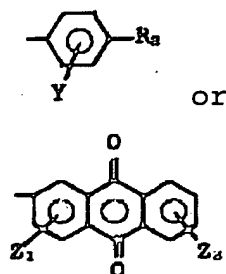
Toner for Developing Electrical Latent Image.

2. Scope of patent claims

The toner for developing electrical latent image has the characteristic of containing the compound shown by the general formula given below and metal-containing dye in the binder resin.



Wherein, X shows substitution radical shown by



R₁ shows hydrogen or alkyl radical, R₂ shows hydrogen, alkyl radical, hydroxyl radical, phenyl radical or phenyl radical possessing substitution radical (hydroxyl radical, halogen atom, alkyl radical etc.), sulfone radical, or its salt with alkali metal, alkaline earth metal or ammonium ion, aliphatic ammonium ion, alicyclic ammonium ion, restrained (?) cyclic ammonium ion etc., Y shows hydrogen, halogen atom, hydroxyl radical, alkyl radical, sulfone radical or its salt with alkali metal, alkaline earth metal, ammonium ion, aliphatic ammonium ion, alicyclic ammonium ion, restrained (?) cyclic ammonium ion etc., Z₁ and Z₂ independently show hydrogen, hydroxyl radical or alkyl radical.

3. Detailed description of the invention

The present invention relates to the toner, particularly the toner used for developing electrical latent image.

Static printing method or electronic photograph method are known as the methods to form visible picture by developing electrical latent image using toner. For example, as regards the electronic photograph method, different methods described in American Patent number 2297691, Patent number Sho 42 - 23910, Sho 43 - 24748 are known.

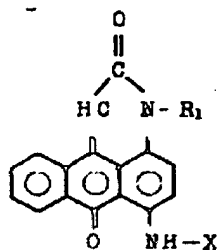
Generally, electrical latent image is formed on the photosensitive material showing light guiding electrical property, by different methods using light guiding electrical substance and then, the latent image mentioned above is developed by using a toner and visible image is obtained, or powder image is transferred on a paper etc. as per requirement and then it is fixed by heating, applying pressure or solvent evaporation etc. and the visible image is obtained. Moreover, as regards the toner used for developing electrical latent image, particles obtained by

finely pulverizing the material formed by dispersing colorant (dye pigment such as carbon black etc.) in the binder resin such as polystyrene etc., into 1 ~ 30 ? is used. This toner is mixed with carrier such as common glass beads, iron powder, flour etc. and 2-component developing method is used for developing electrical latent image.

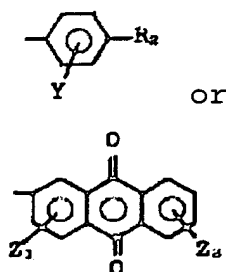
Moreover, method of using insulating magnetic toner is also known like jumping developing method described in Patent Sho 54 - 42141. This method has the advantage of toner being stable and operation being simple as compared to the 1-component developing method known as magnetite method and moreover, photograph can be transferred to the paper. However, the only one disadvantage of this developing method is that it is extremely sensitive to change in humidity of environment. The main reason being extreme sensitivity of surface charge that is one of the required properties of toner in the developing and photographic process, towards change in humidity of environment.

The present invention has been devised to solve the problem of surface charge of toner caused by change in humidity. Therefore, the present invention aims at offering a toner having surface charge property that is stable under the changing humid conditions.

The aim of the present invention is achieved by containing metal-containing dye and the compound shown by the general formula given below in the binder resin.



Wherein, X shows substitution radical shown by



R₁ shows hydrogen or alkyl radical, R₂ shows hydrogen, alkyl radical, hydroxyl radical, phenyl radical or phenyl

radical possessing substitution radical (hydroxyl radical, halogen atom, alkyl radical etc.), sulfone radical, or its salt with alkali metal, alkaline earth metal or ammonium ion, aliphatic ammonium ion, alicyclic ammonium ion, restrained (?) cyclic ammonium ion etc., Y shows hydrogen, halogen atom, hydroxyl radical, alkyl radical, sulfone radical or its salt with alkali metal, alkaline earth metal, ammonium ion, aliphatic ammonium ion, alicyclic ammonium ion, restrained (?) cyclic ammonium ion etc., Z₁ and Z₂ independently show hydrogen, hydroxyl radical or alkyl radical.

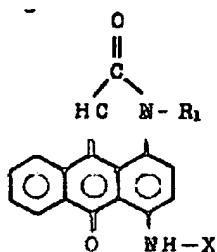
The composition components of the toner of the present invention have been explained in details.

Well-known resins can be used as the binder resin used in toner, for example, styrene group resins (styrene or homo polymer or copolymer containing styrene substitute) such as polystyrene, chloro polystyrene, poly - ? - methyl styrene, styrene - chloro styrene copolymer, styrene -

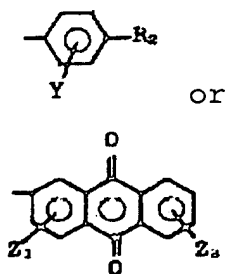
propylene copolymer, styrene - butadiene copolymer, styrene - vinyl chloride copolymer, styrene - vinyl acetate copolymer, styrene - maleic acid copolymer, styrene - acrylic acid ester copolymer (styrene - methyl acrylate copolymer, styrene - ethyl acrylate copolymer, styrene - butyl acrylate copolymer, styrene - phenyl acrylate copolymer etc.), styrene - methacrylic acid ester copolymer (styrene - methyl methacrylate copolymer, styrene - ethyl methacrylate copolymer, styrene - butyl methacrylate copolymer, styrene - phenyl methacrylate copolymer etc.), styrene - ? - chloro methyl acrylate copolymer, styrene - acrylonitrile - acrylic acid ester copolymer etc., vinyl chloride resin, ethylene - vinyl acetate copolymer, rosin denatured maleic acid resin, phenyl resin, epoxy resin, polyester resin, low molecular weight polyethylene, low molecular weight polypropylene, ionomer resin, polyurethane resin, silicone resin, ketone resin, ethylene - ethyl acrylate copolymer, xylene resin, polyvinyl butyral

resin etc. can be given, however, styrene group resins, polyethylene resin, polyester resin, silicone resin, epoxy resin are desired to be used in the present invention. Moreover, these resins can be used independently or as a mixture.

The important compound which is one of the composition components of toner of the present invention is the compound shown by the general formula given below.



[Wherein, X shows substitution radical shown by

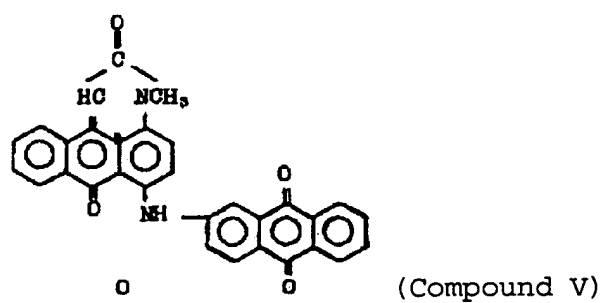
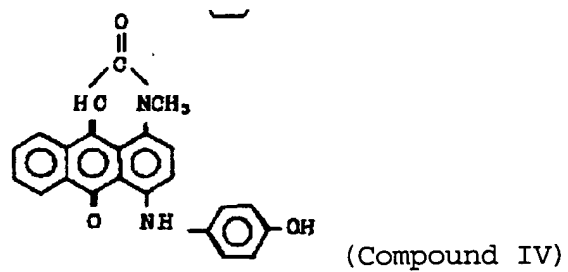
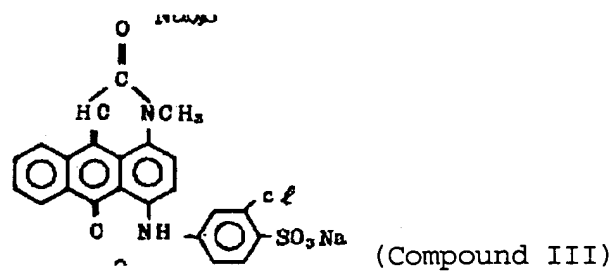
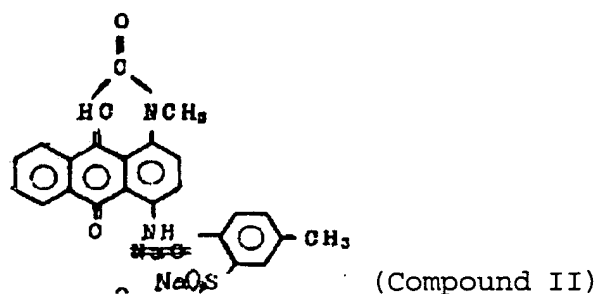
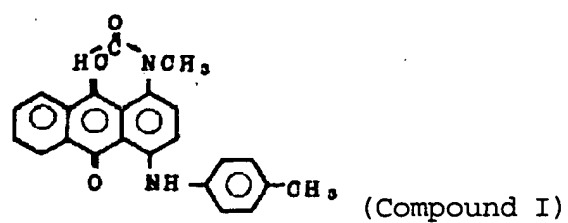


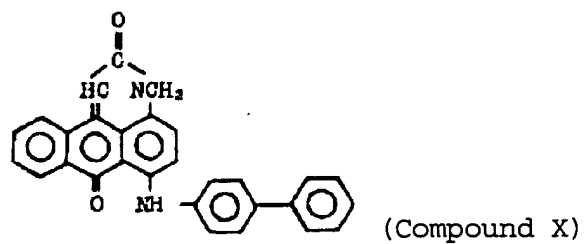
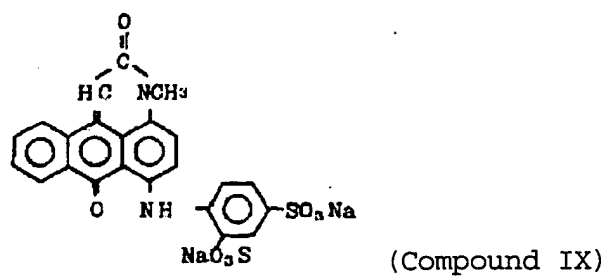
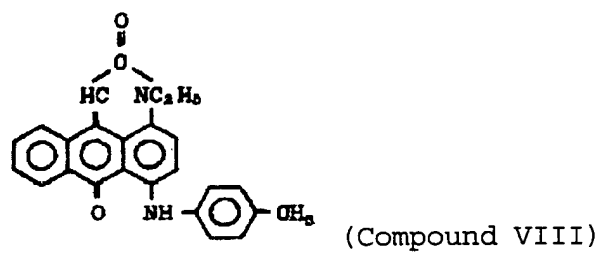
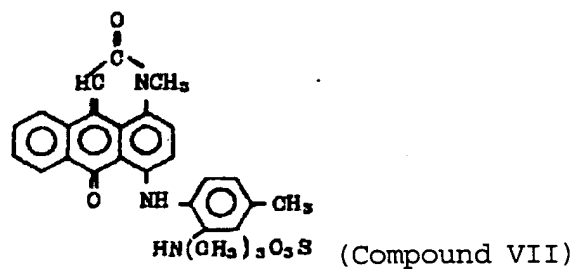
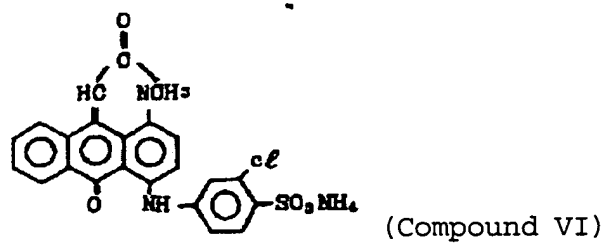
R_1 shows hydrogen or alkyl radical, R_2 shows hydrogen, alkyl radical, hydroxyl radical, phenyl radical or phenyl

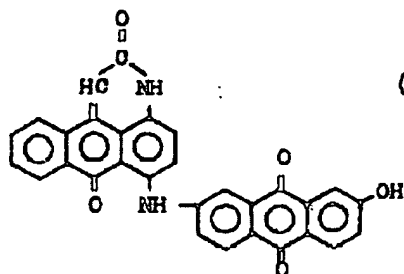
radical possessing substitution radical (hydroxyl radical, halogen atom, alkyl radical etc.), sulfone radical, or its salt with alkali metal, alkaline earth metal or ammonium ion, aliphatic ammonium ion, alicyclic ammonium ion, restrained (?) cyclic ammonium ion etc., Y shows hydrogen, halogen atom, hydroxyl radical, alkyl radical, sulfone radical or its salt with alkali metal, alkaline earth metal, ammonium ion, aliphatic ammonium ion, alicyclic ammonium ion, restrained (?) cyclic ammonium ion etc., Z₁ and Z₂ independently show hydrogen, hydroxyl radical or alkyl radical.]

This compound is contained in the binder resin along with the metal-containing dye based on which surface charge property that is stable against humidity change is imparted.

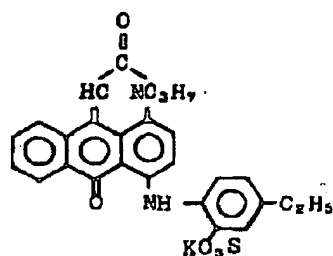
In the present invention, concrete examples of the compound have been given below.



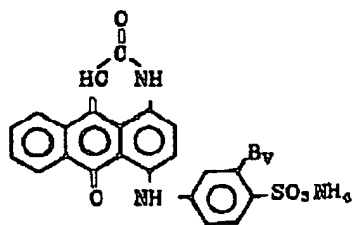




(Compound XI)



(Compound XII)



(Compound XIII)

In the present invention, the compound shown by the general formula given above is not restricted to the concrete examples given below and moreover, these compounds can be used as mixture of 2 or more types.

Next, as regards the metal-containing dye used as charge controlling agent in the present invention, metal-containing dye described in Patent number Sho 53 - 127726 such as Cr, Ni, Co etc. complexes of 3, 5 - di tertiary

butyl - salicylic acid (metal complex salicylic acid or alkyl salicylic acid) are desired, however, azo group oil-soluble dye containing metal complex compound described in Patent number Sho 45 - 26478 such as zapon black RE, pari (?) fast black # 3804 etc. can be used.

The quantity of addition of metal-containing dye should be within the range from 0.1 ~ 10 (weight) with respect to binder resin. Furthermore, in the present invention, other colorant can be jointly used in addition to the compound mentioned above. As regards this colorant, different well-known pigments can be used. For example, carbonblack, nigrosin, iron black, aniline red, brilliant carmine 6B, quinalidone, 2, 9 - di methyl quinalidone, xanthene group dyes and their lake etc. can be given.

There is no particular restriction over the quantity with which the previously exemplified compound (shown by the general formula) is used, and its usage quantity can be determined as per the desired surface charge stability

taking into consideration charge property of binder resin, type of the binder used and other conditions. It is generally used with the quantity of approximately 0.1 ~ 10 (weight) % with respect to binder resin.

If it is less than 0.1 (weight) %, the effect of stabilizing the charge is insufficient whereas it exceeds 10 (weight) %, then effect of stabilizing the charge lowers which is not desired.

The present invention has been explained below in further details with the help of practical examples. Moreover, comparative examples have also been given for clarifying the effect of the present invention.

Practical example 1

100 parts by weight of polystyrene resin, 6 parts by weight of carbon black, 2 parts by weight of compound 1 exemplified above and 2 parts by weight of 3, 5 - di tertiary butyl - salicylic acid chromium chelate were mixed and pulverized in a ball mill after which these were fused and kneaded

in a roll mill. After cooling, coarse pulverizing was performed using hammer mill and then fine pulverizing was performed by air jet method. The obtained fine powder was divided and 3 ~ 20 μ was chosen and toner was prepared. 90 parts by weight of carrier iron powder (product name EFV 200/300, Nihon Teppobun (Japan Iron Powder) make) was mixed with 10 parts by weight of this toner and developing agent was prepared.

Torbo (?) charge in this developing agent was measured when it was - 6.0 μ e/g. Moreover, measurement of torbo (?) charge was performed by blow off method [details have been described in Yohashi (?) Edition of Denshi Shashin Gakka (Electronic Photography Society (1975, 5] . Moreover, torbo (?) charge was measured by the same method in the practical examples and comparative examples given below.

Copying was performed using this developing agent by dry type popular paper electronic photography machine (product name NP1200: Canon K.K. make) when vivacious black colored

image with no fogging was obtained. Moreover, 30000 copies were continuously copied, however, no lowering of quality of copied picture was observed. Properties of this toner did not deteriorate even after keeping it at 40°C and 87 % RH for 1 year.

Practical example 2

Composition was changed to

Styrene - methyl acrylate copolymer	80 (weight) part
Styrene - maleic acid copolymer	20 (weight) parts
Carbon black	10 (weight) parts
Compound (II) exemplified above	4 (weight) parts
3, 5 - di tertiary butyl salicylic acid chromium chelate	2 (weight) parts

and procedure similar to practical example 1 was carried out and vivacious black colored image with no fogging was obtained.

Furthermore, exactly similar image was obtained even at

40°C 87 % RH.

Torbo (?) charge of the toner was - 6.5 ?e/g.

Practical examples 3 ~ 10

Toner composition was changed to that given in table.

Other than this change, procedure similar to practical example 1 was carried out and vivacious black colored image with no fogging was obtained. Moreover, exactly similar image was obtained even at 40°C 87 % RH. Torbo (?) charge of the toner has been given in table.

Practical example	Toner composition (weight) parts	Torbo (?) charge (?e/g)
3	Styrene - butadiene copolymer 100 Carbon black 10 Compound IV exemplified above 3 3, 5 - di tertiary butyl - salicylic acid nickel complex 2	- 5.4
4	Styrene -butyl methacrylate copolymer 90	- 5.1

	<p>Polyvinyl butyral 10</p> <p>Carbon black 8</p> <p>Compound V exemplified above 3</p> <p>Mono tertiary butyl - salicylic acid chromium complex 2</p>	
5	<p>Epoxy resin 70</p> <p>Silicone resin 30</p> <p>Carbon black 6</p> <p>Compound VI exemplified above 2</p> <p>Zapon black RE 2</p>	- 5.0
6	<p>Polyester resin 80</p> <p>Silicone resin 20</p> <p>Carbon black 10</p> <p>Compound II exemplified above 4</p> <p>3, 5 - di tertiary butyl - salicylic acid chromium complex 2</p>	- 7.6
7	<p>Phenol resin 50</p> <p>Polyester resin 50</p> <p>Carbon black 4</p>	- 5.0

	Compound IX exemplified above 0.5 3, 5 - di tertiary butyl - salicylic acid chromium complex 2	
8	Polystyrene 50 Polyester resin 50 Nig rosin 5 Compound II exemplified above 4 pari (?) fast black # 3804 2	- 4.0
9	Styrene - maleic acid copolymer 90 Silicone resin 10 Carbon black 6 Compound X exemplified above 3 3, 5 - di tertiary butyl - salicylic acid chromium complex 2	- 5.9
10	Polyester resin 80 Rosin denatured maleic acid resin 20 Carbon black 3 Nig rosin 3 Compound VII exemplified above 5	- 4.1

	Mono tertiary butyl salicylic acid chromium complex 2	
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Practical example 11

Toner composition was changed to

Polystyrene resin	100 (weight) part
Magnetite	50 "
3, 5 - di tertiary butyl salicylic acid chromium chelate	2 (weight) parts
Compound VII exemplified above	2 "

and procedure similar to practical example 1 was carried out and toner was prepared and 2 % of hydrophobic colloidal silica was added to the toner and copying was performed using dry type popular paper electronic photograph machine (product name NP1200: Canon K.K. make) when vivacious black colored image with no fogging was obtained. Moreover, 50000 copies were continuously copied, however, no deterioration of quality of copied picture was observed and this toner was kept at 40°C 87 % RH, however, no change in image was

observed. Properties of this toner did not deteriorate even after keeping it under the conditions mentioned above for 1 year.

Practical example 12 ~

Toner composition was changed to that given in table. Other than this change, procedure similar to practical example 11 was carried out and vivacious black colored image with no fogging was obtained. Moreover, exactly similar image was obtained even at 40°C 87 % RH. Torbo (?) charge of the toner has been given in table.

Practical example	Toner composition (weight) parts	Torbo (?) charge (e/g)
12	Polystyrene 100 Magnetite 50 Compound II exemplified above 2 3, 5 - di tertiary butyl - salicylic acid chromium complex 2	- 15.8

13	<p>Polystyrene resin 100</p> <p>Compound II exemplified above 6</p> <p>Magnetite 50</p> <p>3, 5 - di tertiary butyl - salicylic acid chromium complex 2</p>	- 12.0
14	<p>Styrene - butadiene copolymer 80</p> <p>Polyester resin 20</p> <p>Magnetite 50</p> <p>Compound IX exemplified above 5</p> <p>Mono tertiary butyl salicylic acid chromium chelate 2</p>	- 10.2
15	<p>Polyethylene resin 70</p> <p>Magnetite 30</p> <p>Compound I exemplified above 2</p> <p>3, 5 - di tertiary butyl - salicylic acid chromium complex 2</p>	- 15.6
16	<p>Styrene - butyl methacrylate 50</p> <p>Polystyrene resin 50</p> <p>Magnetite 50</p>	- 17.3

	Compound II exemplified above 2 3, 5 - di tertiary butyl - salicylic acid chromium complex 2	
17	Epoxy resin 30 Silicone resin 70 Magnetite 50 Compound V exemplified above 10 3, 5 - di tertiary butyl - salicylic acid chromium complex 2	- 16.5

Comparative example 1

Composition was changed to

Polystyrene resin	100 (weight) part
Carbon black	6 "
3, 5 - di tertiary butyl salicylic acid chromium chelate	2 "

and procedure similar to practical example 1 was carried out when at 30°C and 90 % RH, fogging occurred and concentration also remarkably lowered and vivacious image

could not be obtained.

Furthermore, torbo (?) charge of the toner at this time was - 3.3 ?e/g.

Comparative example 2

Composition was changed to

Polyethylene resin	100 (weight) part
Magnetite	50 "
3, 5 - di tertiary butyl salicylic acid chromium chelate	2 "

and procedure similar to practical example 11 was carried out when at 35°C and 85 % RH, fogging occurred and image concentration also remarkably lowered and vivacious image could not be obtained.

Furthermore, torbo (?) charge of the toner at this time was - 3.3 ?e/g.

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